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PRO-FRAGRANCES

5

FIELD OF THE INVENTION

10 The present invention relates to fragrance delivery systems which comprise aldehyde and ketone releasing pro-fragrances, *inter alia*, oxazolidines, β -amino compounds, said pro-fragrances capable of delivering fragrance raw material aldehydes and ketones, to a *situs*, especially to human skin. The pro-fragrances of the present invention are formulatable with both other pro-fragrances and pro-accords as well as fragrance raw materials and pre-blended fragrance mixtures, for example, fragrance accords. The fragrance raw material delivery systems
15 of the present invention provide the user with extended aesthetic benefits.

BACKGROUND OF THE INVENTION

20 Humans have applied scents and fragrances to their skin since antiquity. Originally these aesthetically pleasing materials were commonly isolated in raw form as resins, gums or essential oils from natural sources, *inter alia*, the bark, roots, leaves and fruit of indigenous plants. These resins, gums, and oils were directly applied to the body or diluted with water or other solvent, including in some cases, wine. With the advent of modern chemistry, individual components responsible for the odor properties of these resins, gums and oils were isolated and subsequently characterized. Aside from common "perfume vehicles" *inter alia*, fine perfumes, colognes, eau
25 de toilettes, and after-shave lotions, a wide variety of personal care or personal hygiene items also deliver for aesthetic reasons fragrance notes, accords, or fragrance "characteristics".

It is well known that mixtures of perfume or fragrance raw materials when deposited on the skin lose intensity and may change character with time, mainly due to factors such as differential evaporation and skin penetration. Many attempts have been made to minimize these
30 drawbacks, but so far without notable success. Particularly, efforts have been made to prolong the diffusion, as well as to improve other characteristics of fragrance materials, by e.g. increasing the fragrance raw material concentration or by using additives such as silicones, glycerol, polyethylene glycols and so on. Such additions, however, have never been adequate to increase the longevity of the fragrance odor.

Recently the advent of pro-fragrance and pro-accords have afforded the fine fragrance and perfume formulator with the ability to deliver fragrance raw materials to human skin in a controllable manner thus enhancing the longevity of the fragrance. Most pro-accords *inter alia* orthoesters, are suitable for delivery of fragrance raw material alcohols and esters. Aldehydes and ketones have been delivered via acetals and ketals respectively, however, both of these pro-fragrance materials depend upon the modification of the carbonyl moiety and the rate of ketone fragrance raw material release has been difficult to fine tune to the subtleties of fine fragrance and perfume accords.

Accordingly, there remains a need in the art for a fragrance delivery system which is capable of delivering aldehyde and ketone fragrance raw material releasing pro-fragrance which can be formulated into fine fragrances, perfumes, personal care and personal hygiene products wherein the aldehyde and ketone fragrance raw material components can be released in a highly controllable manner to provide enhanced fragrance longevity.

SUMMARY OF THE INVENTION

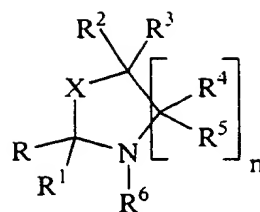
The present invention meets the aforementioned needs in that it has been surprisingly discovered that certain aldehyde fragrance raw materials, *inter alia*, para-t-bucinal, cymal, and lillial can be controllably released from novel heterocyclic pro-fragrances. The heterocyclic pro-fragrances, preferably oxazolidine pro-fragrances, of the present invention are useful in fragrance delivery systems which deliver fine fragrances with an enhanced perfume longevity.

A first aspect of the present invention relates to fragrance delivery systems which comprise pro-fragrances or pro-accords selected from at least two of the following:

- i) aldehyde and ketone releasing pro-fragrances, preferably an oxazolidine pro-fragrances;
- ii) β -amino pro-fragrances; and
- iii) orthoester pro-accords.

The fragrance delivery systems of the present invention comprise:

- A) from about 0.01% by weight, of a pro-fragrance component comprising:
 - a) optionally at least 0.01% by weight, of an aldehyde or ketone releasing pro-fragrance component, said pro-fragrance having the formula:



wherein said pro-fragrance or pro-accord releases an aldehyde or a ketone fragrance raw material, wherein X is oxygen or sulfur; R is:

- i) C₆-C₂₂ substituted or unsubstituted linear alkyl;
- ii) C₆-C₂₂ substituted or unsubstituted branched alkyl;
- iii) C₆-C₂₂ substituted or unsubstituted linear alkenyl;
- iv) C₆-C₂₂ substituted or unsubstituted branched alkenyl;
- v) C₆-C₂₂ substituted or unsubstituted cycloalkyl;
- vi) C₆-C₂₂ substituted or unsubstituted branched cycloalkyl;
- vii) C₆-C₂₂ substituted or unsubstituted cycloalkenyl;
- viii) C₆-C₂₂ substituted or unsubstituted branched cycloalkenyl;
- ix) C₆-C₂₂ substituted or unsubstituted aryl;
- x) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- xi) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;
- xii) and mixtures thereof;

R¹ is:

- i) hydrogen;
- ii) C₁-C₁₀ substituted or unsubstituted linear alkyl;
- iii) C₃-C₁₀ substituted or unsubstituted branched alkyl;
- iv) C₂-C₁₀ substituted or unsubstituted linear alkenyl;
- v) C₃-C₁₀ substituted or unsubstituted branched alkenyl;
- vi) C₃-C₁₅ substituted or unsubstituted cycloalkyl;
- vii) C₄-C₁₅ substituted or unsubstituted branched cycloalkyl;
- viii) C₄-C₁₅ substituted or unsubstituted cycloalkenyl;
- ix) C₅-C₁₅ substituted or unsubstituted branched cycloalkenyl;
- x) C₆-C₁₅ substituted or unsubstituted aryl;
- xi) C₆-C₂₂ substituted or unsubstituted heterocyclicalkyl;
- xii) C₆-C₂₂ substituted or unsubstituted heterocyclicalkenyl;

R and R¹ can be taken together to form a substituted or unsubstituted ring having in the ring from 3 to 10 carbon atoms; and

each R^2 , R^3 , R^6 and each R^4 and R^5 pair are independently:

- i) R^1 ;
- ii) hydroxyl;
- iii) a carbonyl comprising unit having the formula:



wherein R^7 is:

- a) -OH;
 - b) $-OR^8$ wherein R^8 is hydrogen, C_1 - C_{15} substituted or unsubstituted linear alkyl, C_1 - C_{15} substituted or unsubstituted branched alkyl, C_2 - C_{22} substituted or unsubstituted linear alkenyl, C_3 - C_{22} substituted or unsubstituted branched alkenyl, or mixtures thereof; or R^8 is M, wherein M is a water soluble cation of sufficient charge to render neutrality;
 - c) $-N(R^9)_2$ wherein R^9 is hydrogen, C_1 - C_6 substituted or unsubstituted linear alkyl, C_3 - C_6 substituted or unsubstituted branched alkyl, or mixtures thereof;
 - d) C_1 - C_{22} substituted or unsubstituted linear alkyl;
 - e) C_1 - C_{22} substituted or unsubstituted branched alkyl;
 - f) C_2 - C_{22} substituted or unsubstituted linear alkenyl;
 - g) C_3 - C_{22} substituted or unsubstituted branched alkenyl;
 - h) C_3 - C_{22} substituted or unsubstituted cycloalkyl;
 - i) C_6 - C_{22} substituted or unsubstituted aryl;
 - j) C_6 - C_{22} substituted or unsubstituted heterocyclicalkyl;
 - k) C_6 - C_{22} substituted or unsubstituted heterocyclicalkenyl;
- the index x is from 0 to 22;

- iv) alkyleneoxy units having the formula:



wherein each R^{10} , R^{11} , and R^{12} is independently;

- a) hydrogen;
- b) -OH;
- c) C_1 - C_4 alkyl;

d) or mixtures thereof;

R¹³ is:

a) hydrogen;

b) C₁-C₄ alkyl;

c) or mixtures thereof;

R¹⁴ is:

a) hydrogen;

b) C₁-C₄ alkyl;

c) or mixtures thereof;

R¹⁰ and R¹¹ can be taken together to form a C₃-C₆ spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50;

v) any two R², R³, R⁴, R⁵, or R⁶ units can be taken together to form:

a) a carbonyl moiety;

b) a C₃-C₆ spiroannulated ring;

c) a heterocyclic aromatic ring comprising from 5 to 7 atoms;

d) a non-heterocyclic aromatic ring comprising from 5 to 7 atoms;

e) a heterocyclic ring comprising from 5 to 7 atoms;

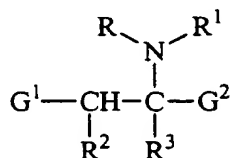
f) a non-heterocyclic ring comprising from 5 to 7 atoms;

g) or mixtures thereof;

vi) and mixtures thereof; and

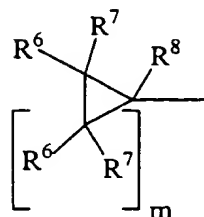
the index n is an integer from 1 to 3;

b) optionally at least 0.01% by weight, of an β -amino pro-fragrance component, said pro-fragrance having the formula:



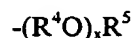
wherein G¹ is C₁-C₄ alkyl, -CN, -C(O)Y¹, -CO₂Y¹, Y², and mixtures thereof; G² is C₁-C₄ alkyl, -CN, -C(O)Y¹, -CO₂Y¹, Y², and mixtures

thereof; Y^1 and Y^2 are each independently C_1 - C_4 alkyl, or a unit having the formula:



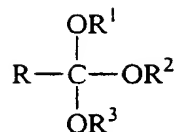
wherein R^6 , R^7 , and R^8 are each independently hydrogen, C_1 - C_4 alkyl, and mixtures thereof; R^6 and R^7 can be taken together to form an exocyclic double bond with the ring; any two R^6 and R^7 , or an R^6 and R^7 with an R^8 can be taken together to form an endocyclic double bond within the ring; two or more R^6 , R^7 , and R^8 units may be taken together to form one or more C_3 - C_7 fused rings, bicyclic rings, or spiroannular rings; m is from 1 to 5;

provided one G^1 or G^2 is $-C(O)Y^1$, $-CO_2Y^1$, or $-CN$; R and R^1 are each independently hydrogen, C_1 - C_{22} substituted or unsubstituted, branched or unbranched alkyl, C_2 - C_{22} substituted or unsubstituted, branched or unbranched alkenyl, C_2 - C_{20} substituted or unsubstituted, branched or unbranched hydroxyalkyl, C_7 - C_{20} substituted or unsubstituted alkylenearyl, C_3 - C_{20} substituted or unsubstituted cycloalkyl, alkyleneoxy units having the formula:

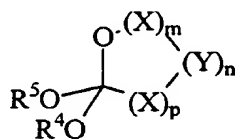


wherein R^4 is C_2 - C_4 alkylene, R^5 is hydrogen, C_1 - C_4 alkyl, and mixtures thereof, x is from 1 to 6; C_6 - C_{20} aryl, C_5 - C_{20} heteroaryl comprising one or more heteroatoms selected from the group consisting of nitrogen, oxygen, sulfur, and mixtures thereof; R and R^1 can be taken together to form one or more aromatic or non-aromatic, heterocyclic or non-heterocyclic, single rings, fused rings, bicyclo rings, spiroannulated rings, or mixtures thereof, said rings comprising from 2 to 20 carbon atoms and one or more heteroatoms selected from the group consisting of nitrogen, oxygen, sulfur, and mixtures thereof;

- c) optionally at least 0.01% by weight, of an orthoester pro-accord having the formula:



wherein R is hydrogen, C₁-C₈ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ substituted or unsubstituted aryl, and mixtures thereof; R¹, R² and R³ are independently C₁-C₂₀ linear, branched, or substituted alkyl; C₂-C₂₀ linear, branched, or substituted alkenyl; C₅-C₂₀ substituted or unsubstituted cyclic alkyl; C₆-C₂₀ substituted or unsubstituted aryl, C₂-C₄₀ substituted or unsubstituted alkyleneoxy; C₃-C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆-C₄₀ substituted or unsubstituted alkylenearyl; C₆-C₃₂ substituted or unsubstituted aryloxy; C₆-C₄₀ substituted or unsubstituted alkyleneoxyaryl; C₆-C₄₀ oxyalkylenearyl, and mixtures thereof; or a cyclic orthoester having the formula:



wherein at least one R⁴ or R⁵ is derived from a fragrance raw material alcohol, each X is -C(R⁶)₂- wherein each R⁶ is independently hydrogen, C₁-C₂₂ linear or branched alkyl, C₂-C₂₂ linear or branched alkenyl, C₆-C₂₂ substituted or unsubstituted aryl, and mixtures thereof, Y is -CR⁷R⁸-, C=O, and mixtures thereof, wherein R⁷ and R⁸ are independently hydrogen, hydroxyl, nitro, nitrilo, C₁-C₃₀ substituted or unsubstituted linear alkyl, C₃-C₃₀ substituted or unsubstituted branched alkyl, C₃-C₃₀ substituted or unsubstituted cyclic alkyl, C₂-C₃₀ substituted or unsubstituted linear alkenyl, C₃-C₃₀ substituted or unsubstituted branched alkenyl, C₃-C₃₀ substituted or unsubstituted cyclic alkenyl, C₂-C₃₀ substituted or unsubstituted linear alkynyl, C₃-C₃₀ substituted or unsubstituted branched alkynyl, C₆-C₃₀ substituted or unsubstituted alkylenearyl, C₆-C₃₀ substituted or unsubstituted aryl, C₂-C₂₀ substituted

or unsubstituted alkyleneoxy, C₃-C₂₀ substituted or unsubstituted alkyleneoxyalkyl, C₇-C₂₀ substituted or unsubstituted alkylenearyl, C₆-C₂₀ substituted or unsubstituted alkyleneoxyaryl, and mixtures thereof, or R⁷ and R⁸ can be taken together to form a spiroannulated ring or taken together with any R⁶ to form a fused ring, said spiroannulated or fused ring having from 3 to 8 carbons and optionally one or more heteroatoms in said ring, said ring further optionally substituted by one or more C₁-C₂₂ alkyl, C₁-C₂₂ alkenyl, C₆-C₁₂ aryl, C₆-C₂₂ alkylenearyl units, and mixtures thereof; m is from 0 to 14, p is from 0 to 14, and n is from 0 to 3; provided m + n + p is at least 1 and less than or equal to 14; and

- B) optionally from about 1% by weight, a fragrance raw material component comprising:
- i) optionally at least 1% by weight, of a mixture of one or more base note fragrances;
 - ii) optionally at least 1% by weight, of a mixture of one or more top or middle note fragrances;
 - iii) optionally the balance carriers, fixatives, and other adjunct ingredients.

These and other objects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims. All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (° C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to fragrance delivery systems which comprise at least two pro-fragrances or pro-accords wherein at least one pro-fragrance or pro-acord is selected from two of the following groups:

- i) aldehyde and ketone releasing pro-fragrances, preferably an oxazolidine pro-fragrances;
- ii) β-amino pro-fragrances; and
- iii) orthoester pro-accords.

Therefore, the fragrance delivery systems of the present invention comprise at least one pro-fragrance or pro-acord from group (i) and one from group (ii); or one from group (i) and one

from (iii); or one from group (ii) and one from group (iii). However, one or more pro-fragrances or pro-accords may be selected from each group or several from two groups.

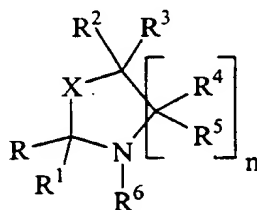
One preferred embodiment comprises a fragrance delivery system which comprises all three pro-fragrance and pro-accords groups. Optionally, and preferably, the fragrance delivery systems of the present invention comprise other fragrance raw materials. In addition, the fragrance raw material delivery systems are typically admixed with one or more carriers or fixatives. The pro-fragrances and pro-accords of the present invention are suitable for use in fragrance delivery systems which are capable in delivering enhanced fragrance benefits to fine fragrances and perfumes as well as personal care and personal hygiene articles.

The following is a description of the essential pro-fragrances or pro-accords of the present invention.

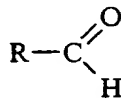
Aldehyde and Ketone Releasing Pro-fragrances

The fragrance delivery systems of the present invention may comprise from about 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 99%, more preferably to about 75%, most preferably to about 50% by weight, of one or more heterocyclic aldehyde-releasing and/or ketone-releasing pro-fragrances, preferably oxazolidines, tetrahydro-1,3-oxazines, thiazolidines, or tetrahydro-1,3-thiazines, more preferably oxazolidines, or tetrahydro-1,3-oxazines, most preferably oxazolidines.

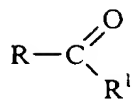
The pro-fragrances or pro-accords which are suitable for use in the fragrance delivery systems described herein have the formula:



and are capable of releasing an aldehyde fragrance raw material having the formula:



or a ketone fragrance raw material having the formula:



For the purposes of the fragrance delivery systems which comprise one or more heterocyclic pro-fragrances or pro-accords, R units are defined herein as:

- i) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₅ substituted or unsubstituted linear alkyl; one or more examples of a fragrance raw material which comprises this unit includes nonanal and decanal;
- ii) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₅ substituted or unsubstituted branched alkyl; one or more examples of a fragrance raw material which comprises this unit includes 2-methyldecanal;
- iii) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₅ substituted or unsubstituted linear alkenyl; one or more examples of a fragrance raw material which comprises this unit includes 10-undecenal;
- iv) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₅ substituted or unsubstituted branched alkenyl; one or more examples of a fragrance raw material which comprises this unit includes citral, melonal, and neral;
- v) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₀ substituted or unsubstituted cycloalkyl; one or more examples of a fragrance raw material which comprises this unit includes cyclopentadecanone;
- vi) C₆-C₂₂, preferably C₆-C₁₅, more preferably C₆-C₁₅ substituted or unsubstituted branched cycloalkyl; one or more examples of a fragrance raw material which comprises this unit includes camphor and muscone;
- vii) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₅ substituted or unsubstituted cycloalkenyl; one or more examples of a fragrance raw material which comprises this unit includes civetone;
- viii) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₅ substituted or unsubstituted branched cycloalkenyl; one or more examples of a fragrance raw material which comprises this unit includes α-damascone and β-ionone;
- ix) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₀ substituted or unsubstituted aryl wherein said aryl unit preferably comprises a phenyl unit; one or more examples of a fragrance raw material which comprises this unit includes benzaldehyde, hydrotropaldehyde and vanillin;

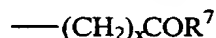
- x) C₆-C₂₂, preferably C₆-C₁₅, more preferably C₆-C₁₅ substituted or unsubstituted heterocyclicalkyl;
- xi) C₆-C₂₂, preferably C₆-C₁₈, more preferably C₆-C₁₅ substituted or unsubstituted heterocyclicalkenyl; one or more examples of a fragrance raw material which comprises this unit includes;
- xii) and mixtures thereof;

R¹ is:

- i) hydrogen;
- ii) C₁-C₁₀, preferably C₁-C₅ substituted or unsubstituted linear alkyl;
- iii) C₃-C₁₀, preferably C₃-C₅ substituted or unsubstituted branched alkyl;
- iv) C₂-C₁₀, preferably C₂-C₅ substituted or unsubstituted linear alkenyl;
- v) C₃-C₁₀, preferably C₄-C₁₀ substituted or unsubstituted branched alkenyl;
- vi) C₃-C₁₅, preferably C₆-C₁₀ substituted or unsubstituted cycloalkyl;
- vii) C₄-C₁₅, preferably C₆-C₁₀ substituted or unsubstituted branched cycloalkyl;
- viii) C₄-C₁₅, preferably C₆-C₁₀ substituted or unsubstituted cycloalkenyl;
- ix) C₅-C₁₅, preferably C₆-C₁₀ substituted or unsubstituted branched cycloalkenyl;
- x) C₆-C₁₅, preferably C₆-C₁₀ substituted or unsubstituted aryl;
- xi) C₆-C₂₂, preferably C₆-C₁₀ substituted or unsubstituted heterocyclicalkyl;
- xii) C₆-C₂₂, preferably C₆-C₁₀ substituted or unsubstituted heterocyclicalkenyl;

R and R¹ can be taken together to form a substituted or unsubstituted ring having in the ring from 3 to 10 carbon atoms; one or more examples of which are substituted cyclopentanone derivatives inter alia hedione and nectaryl; and each R², R³, R⁶ and each R⁴ and R⁵ pair are independently:

- i) R¹;
- ii) hydroxyl;
- iii) a carbonyl comprising unit having the formula:



wherein R⁷ is:

- a) -OH, in the case of carboxylic acids;
- b) -OR⁸, in the case of esters wherein R⁸ is hydrogen; C₁-C₁₅, preferably C₁-C₁₀, more preferably C₁-C₄ substituted or unsubstituted linear alkyl; C₃-C₁₅, preferably C₃-C₁₀, more preferably C₃-C₄ substituted or unsubstituted branched alkyl; C₂-C₂₂, preferably C₂-C₁₀, more preferably C₂-C₄ substituted or unsubstituted linear alkenyl; C₃-C₂₂ substituted or

unsubstituted branched alkenyl, or mixtures thereof; or R^8 is a cation, M, having sufficient charge to provide electronic neutrality, preferably M is sodium, potassium, and ammonium;

- c) $-N(R^9)_2$ in the case of amides wherein each R^9 is independently hydrogen; C_1-C_{15} , preferably C_1-C_{10} , more preferably C_1-C_4 substituted or unsubstituted linear alkyl; C_3-C_{15} , preferably C_3-C_{10} , more preferably C_3-C_4 substituted or unsubstituted branched alkyl; or mixtures thereof;
- d) C_1-C_{22} , preferably C_1-C_5 substituted or unsubstituted linear alkyl;
- e) C_1-C_{22} , preferably C_3-C_5 substituted or unsubstituted branched alkyl;
- f) C_2-C_{22} , preferably C_2-C_5 substituted or unsubstituted linear alkenyl;
- g) C_3-C_{22} , preferably C_4-C_{10} substituted or unsubstituted branched alkenyl;
- h) C_5-C_{22} , preferably C_6-C_{10} substituted or unsubstituted cycloalkyl;
- i) C_6-C_{22} , preferably C_6-C_{10} substituted or unsubstituted aryl;
- j) C_6-C_{22} , preferably C_6-C_{10} substituted or unsubstituted heterocyclicalkyl;
- k) C_6-C_{22} , preferably C_6-C_{10} substituted or unsubstituted heterocyclicalkenyl;

the index is from 0 to 22;

- v) alkyleneoxy units having the formula:



wherein each R^{10} , R^{11} , and R^{12} is independently;

- a) hydrogen;
- b) $-OH$;
- c) C_1-C_4 alkyl, preferably methyl;
- d) or mixtures thereof; preferably R^{10} , R^{11} , and R^{12} are each hydrogen;

R^{13} is:

- a) hydrogen;
- b) C_1-C_4 alkyl, preferably methyl;
- c) or mixtures thereof; preferably R^{13} is methyl or hydrogen, more preferably hydrogen;

R^{14} is:

- a) hydrogen;
- b) C_1-C_4 alkyl, preferably methyl;

c) or mixtures thereof; preferred R^{14} is hydrogen;
 R^{10} and R^{11} can be taken together to form a C_3 - C_6 spiroannulated ring, carbonyl unit, or mixtures thereof; y has the value from 0 to 10, z has the value from 1 to 50;

vi) any two R^2 , R^3 , R^4 , R^5 , or R^6 units can be taken together, and where feasible, combined to form:

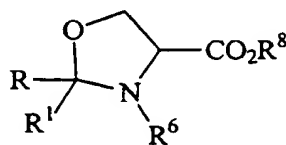
- a) a carbonyl moiety;
- b) a C_3 - C_6 spiroannulated ring;
- c) a heterocyclic aromatic ring comprising from 5 to 7 atoms;
- d) a non-heterocyclic aromatic ring comprising from 5 to 7 atoms;
- e) a heterocyclic ring comprising from 5 to 7 atoms;
- f) a non-heterocyclic ring comprising from 5 to 7 atoms;
- g) or mixtures thereof;

vii) and mixtures thereof;

the index n is an integer from 1 to 3, preferably 1 or 2, more preferably 1.

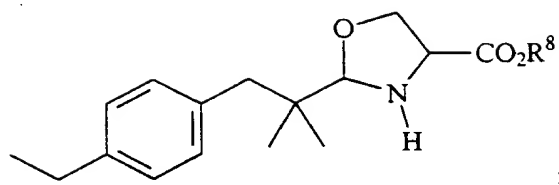
For the purposes of the present invention, the term "substituted" is defined herein as "compatible moieties which replace a hydrogen atom". For the purposes of the present invention, hydrogens which are substitutable are labeled as R' units in the following examples. Non-limiting examples of substituents which can replace hydrogen atoms are C_1 - C_{22} linear or branched hydrocarbyl units, *inter alia*, alkyl, alkenyl; hydroxy, nitrilo, nitro, carboxyl ($-CHO$; $-CO_2H$; $-CO_2R''$; $-CONH_2$; $-CONHR''$; $-CONR''_2$; wherein R'' is C_1 - C_{12} linear or branched alkyl), amino, C_1 - C_{12} mono- and dialkylamino, and mixtures thereof. However, the formulator may wish to include other substituents not specifically mentioned herein. Not each hydrogen of a substituted unit, i.e., substituted linear alkyl, must be substituted; only one hydrogen must be substituted by another moiety for a unit to be "substituted" for the purposes of the present invention.

A non-limiting example of a preferred aldehyde and ketone releasing pro-fragrance has the general formula:

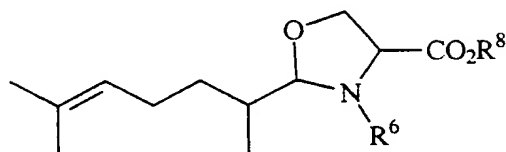


non-limiting examples of which include the pro-fragrances having the formula:

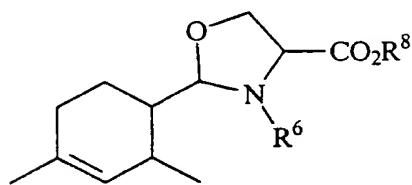
a)



b)



c)

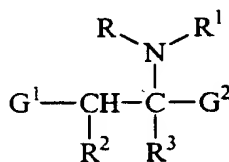


d) and mixtures thereof.

 β -Amino Pro-fragrances

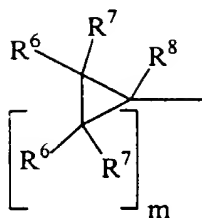
10 The fragrance delivery systems of the present invention may comprise from about 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 99%, more preferably to about 75%, most preferably to about 50% by weight, of one or more β -amino pro-fragrances, preferably ionone and damascone releasing β -amino pro-fragrances.

15 The β -amino pro-fragrances of the present invention have the formula:



wherein G^1 is C_1 - C_4 alkyl, $-\text{CN}$, $-\text{C}(\text{O})\text{Y}^1$, $-\text{CO}_2\text{Y}^1$, Y^2 , and mixtures thereof; G^2 is C_1 - C_4 alkyl, $-\text{CN}$, $-\text{C}(\text{O})\text{Y}^1$, $-\text{CO}_2\text{Y}^1$, Y^2 , and mixtures thereof; Y^1 and Y^2 are each independently C_1 - C_4 alkyl, or a unit having the formula:

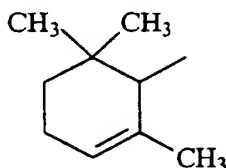
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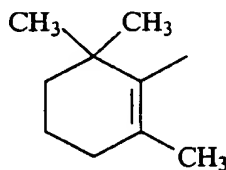
wherein R^6 , R^7 , and R^8 are each independently hydrogen, C_1 - C_4 alkyl, and mixtures thereof; preferably methyl; or alternatively any pair of R^6 and R^7 can be taken together to form an exocyclic double bond with the ring; any two adjacent R^6 and R^7 units, or alternatively an R^6 or R^7 unit with an adjacent R^8 unit can be taken together to form an endocyclic double bond within the ring, preferred compounds comprising endocyclic double bonds include C_6 hydrocarbyl units which include cycloalkyl and cycloalkenyl moieties, *inter alia*, damascones and ionones, further described herein below; or two or more R^6 , R^7 , and R^8 units from any ring carbon may be taken together to form one or more C_3 - C_7 fused rings, bicyclic rings, or spiroannular rings; provided one G^1 or G^2 is $-C(O)Y^1$, $-CO_2Y^1$, or $-CN$. The index m is from 1 to 5; preferably m is 4 which provides a cyclohexyl ring.

Beyond the requirement that at least one G^1 or G^2 unit comprise a $-C(O)Y^1$, $-CO_2Y^1$, or $-CN$ unit, preferred G^1 and G^2 units are C_1 - C_4 alkyl, preferably methyl; and a unit wherein Y^1 is selected from the group consisting of:

- i) 2,6,6-trimethylcyclohex-2-enyl having the formula:

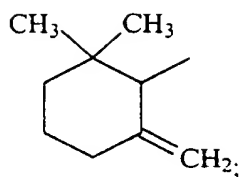


- ii) 2,6,6-trimethylcyclohex-1-enyl having the formula:

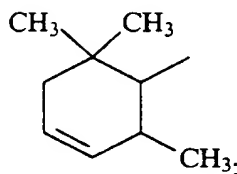


- iii) 2-methylene-6,6-dimethylcyclohexanyl having the formula:

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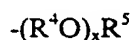
iv) 2,6,6-trimethylcyclohex-3-enyl having the formula:



v) and mixtures thereof.

Further non-limiting examples of Y^1 and Y^2 units include 4,6,6-trimethylcyclohex-1-enyl; 2,2-dimethylcyclohexyl; 2,2,4-trimethylcyclohexyl; 2,2,6-trimethylcyclohexyl; 2,2-dimethyl-3-methylene-6-methylcyclohexanyl; 2,2,3,6-tetramethylcyclohexanyl; 2-methyl-6,6-dimethylhexa-1,3-dienyl; 4-methyl-6,6-dimethylhexa-1,3-dienyl; and mixtures thereof.

R and R^1 are each independently hydrogen, C_1 - C_{22} substituted or unsubstituted, branched or unbranched alkyl, C_2 - C_{22} substituted or unsubstituted, branched or unbranched alkenyl, C_2 - C_{20} substituted or unsubstituted, branched or unbranched hydroxyalkyl, C_7 - C_{20} substituted or unsubstituted alkylenearyl, C_3 - C_{20} substituted or unsubstituted cycloalkyl, alkyleneoxy units having the formula:



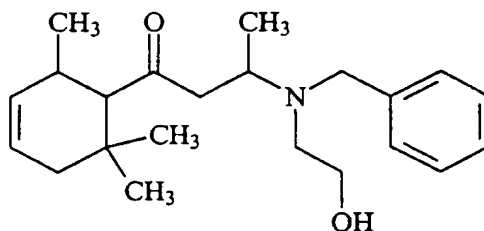
wherein R^4 is C_2 - C_4 alkylene, R^5 is hydrogen, C_1 - C_4 alkyl, and mixtures thereof, x is from 1 to 6; C_6 - C_{20} aryl, C_5 - C_{20} heteroaryl comprising one or more heteroatoms selected from the group consisting of nitrogen, oxygen, sulfur, and mixtures thereof; R and R^1 can be taken together to form one or more aromatic or non-aromatic, heterocyclic or non-heterocyclic, single rings, fused rings, bicyclo rings, spiroannulated rings, or mixtures thereof, said rings comprising from 2 to 20 carbon atoms and one or more heteroatoms selected from the group consisting of nitrogen, oxygen, sulfur, and mixtures thereof.

The following are the common chemical names for the damascones and ionones which are delivered by the pro-fragrances of the present invention; 1-(2,6,6-trimethylcyclohex-2-enyl)-2-butene-1-one (α -damascone), 1-(2,6,6-trimethylcyclohex-1-enyl)-2-butene-1-one (β -damascone), 1-(2-methylene-6,6-dimethylcyclohexanyl)-2-butene-1-one (γ -damascone), 1-(2,6,6-trimethylcyclohex-3-enyl)-2-butene-1-one (δ -damascone), 4-(2,6,6-trimethylcyclohex-2-enyl)-3-

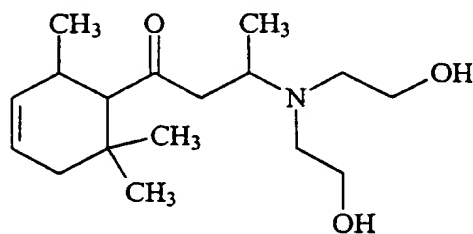
butene-2-one (α -ionone), 4-(2,6,6-trimethylcyclohex-1-enyl)-3-butene-2-one (β -ionone), 4-(2-methylene-6,6-dimethylcyclohexanyl)-3-butene-2-one (γ -ionone).

Further preferred ketones which can be delivered by the β -amino ketone pro-fragrances of the present invention include 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-methyl-3-buten-2-one, 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-1,6-heptadien-3-one, 4-(2,5,6,6-tetramethyl-2-cyclohexen-1-yl)-3-methyl-3-buten-2-one, 2-pentyl-2-cyclopenten-1-one, 2-hexyl-2-cyclopenten-1-one, *cis*-3-methyl-2-(2-pentenyl)-2-cyclopenten-1-one, 6-(2-propenyl)-5-methyl-2-(1-methylethylidene)cyclohexanone, 4-(4-methoxy)phenyl-3-buten-2-one, 2,5,5-trimethyl-2,6-heptadien-4-one, and 2-methyl-6-(4-methylcyclohex-3-enyl)-2,5-heptadien-4-one.

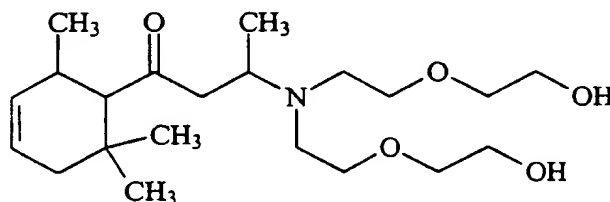
Non-limiting examples of β -amino pro-fragrances according to the present invention include 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-3-N-(2-hydroxyethyl)-N-phenylmethyl-1-butanone having the formula:



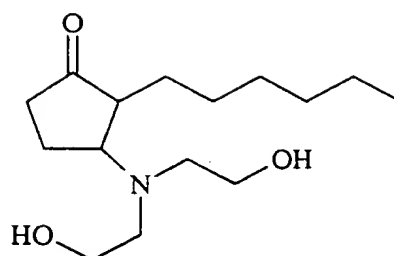
1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-3-N,N-di(2-hydroxyethyl)-1-butanone having the formula:



1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-3-N,N-bis(5-hydroxy-3-oxapentyl)-1-butanone having the formula:

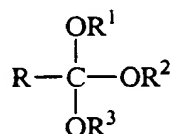


and 2-hexyl-3-di(2-hydroxyethyl)aminocyclopentanone having the formula:

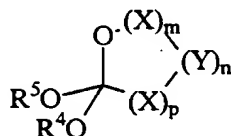


Orthoester Pro-accords

The fragrance delivery systems of the present invention optionally comprise optionally from about 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 99%, more preferably to about 75%, most preferably to about 50% by weight, of an orthoester pro-accord having the formula:



wherein R is hydrogen, C₁-C₈ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ substituted or unsubstituted aryl, and mixtures thereof; R¹, R² and R³ are independently C₁-C₂₀ linear, branched, or substituted alkyl; C₂-C₂₀ linear, branched, or substituted alkenyl; C₅-C₂₀ substituted or unsubstituted cyclic alkyl; C₆-C₂₀ substituted or unsubstituted aryl, C₂-C₄₀ substituted or unsubstituted alkyleneoxy; C₃-C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆-C₄₀ substituted or unsubstituted alkylenearyl; C₆-C₃₂ substituted or unsubstituted aryloxy; C₆-C₄₀ substituted or unsubstituted alkyleneoxyaryl; C₆-C₄₀ oxyalkylenearyl, and mixtures thereof; or a cyclic orthoester having the formula:



wherein at least one R⁴ or R⁵ is derived from a fragrance raw material alcohol, each X is -C(R⁶)₂- wherein each R⁶ is independently hydrogen, C₁-C₂₂ linear or branched alkyl, C₂-C₂₂ linear or branched alkenyl, C₆-C₂₂ substituted or unsubstituted aryl, and mixtures thereof, Y is -CR⁷R⁸-, C=O, and mixtures thereof, wherein R⁷ and R⁸ are independently hydrogen, hydroxyl, nitro, nitrilo, C₁-C₃₀ substituted or unsubstituted linear alkyl, C₃-C₃₀ substituted or unsubstituted

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ol, 2-methyl-4-phenylpentanol (Pamplefleur), 3-methyl-5-phenylpentanol (Phenoxanol), 2-methyl-5-phenylpentanol, 2-methyl-5-(2,3-dimethyltricyclo[2.2.1.0(2,6)]hept-3-yl)-2-penten-1-ol (santalol), 4-methyl-1-phenyl-2-pentanol, (1-methyl-bicyclo[2.1.1]hepten-2-yl)-2-methylpent-1-en-3-ol, 3-methyl-1-phenylpentan-3-ol, 1,2-dimethyl-3-(1-methylethenyl)cyclopentan-1-ol, 2-isopropyl-5-methyl-2-hexenol, *cis*-3-hexen-1-ol, *trans*-2-hexen-1-ol, 2-isopropenyl-4-methyl-4-hexen-1-ol (Lavandulol), 2-ethyl-2-prenyl-3-hexenol, 1-hydroxymethyl-4-iso-propenyl-1-cyclohexene (Dihydrocuminy alcohol), 1-methyl-4-isopropenylcyclohex-6-en-2-ol (carvenol), 6-methyl-3-isopropenylcyclohexan-1-ol, 1-methyl-4-iso-propenylcyclohexan-3-ol, 4-isopropyl-1-methylcyclohexan-3-ol, 4-tert-butylcyclo-hexanol, 2-tert-butylcyclohexanol, 2-tert-butyl-4-methylcyclohexanol, 4-isopropyl-cyclohexanol, 4-methyl-1-(1-methylethyl)-3-cyclohexen-1-ol, 2-(5,6,6-trimethyl-2-norbornyl)cyclohexanol, isobornylcyclohexanol, 3,3,5-trimethylcyclohexanol, 1-methyl-4-isopropylcyclohexan-3-ol, 1,2-dimethyl-3-(1-methylethyl)cyclohexan-1-ol, heptanol, 2,4-dimethylheptan-1-ol, 2,4-dimethyl-2,6-heptandienol, 6,6-dimethyl-2-oxymethylbicyclo[3.1.1]hept-2-ene (myrtenol), 4-methyl-2,4-heptadien-1-ol, 3,4,5,6,6-pentamethyl-2-heptanol, 3,6-dimethyl-3-vinyl-5-hepten-2-ol, 6,6-dimethyl-3-hydroxy-2-methylenebicyclo[3.1.1]heptane, 1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 2,6-dimethylheptan-2-ol, 2,6,6-trimethylbicyclo[1.3.3]heptan-2-ol, octanol, 2-octenol, 2-methyloctan-2-ol, 2-methyl-6-methylene-7-octen-2-ol (myrcenol), 7-methyloctan-1-ol, 3,7-dimethyl-6-octenol, 3,7-dimethyl-7-octenol, 3,7-dimethyl-6-octen-1-ol (citronellol), 3,7-dimethyl-2,6-octadien-1-ol (geraniol), 3,7-dimethyl-2,6-octadien-1-ol (nerol), 3,7-dimethyl-1,6-octadien-3-ol (linalool), 3,7-dimethyloctan-1-ol (pelagrol), 3,7-dimethyloctan-3-ol (tetrahydrolinalool), 2,4-octadien-1-ol, 3,7-dimethyl-6-octen-3-ol, 2,6-dimethyl-7-octen-2-ol, 2,6-dimethyl-5,7-octadien-2-ol, 4,7-dimethyl-4-vinyl-6-octen-3-ol, 3-methyloctan-3-ol, 2,6-dimethyloctan-2-ol, 2,6-dimethyloctan-3-ol, 3,6-dimethyloctan-3-ol, 2,6-dimethyl-7-octen-2-ol, 2,6-dimethyl-3,5-octadien-2-ol (muguol), 3-methyl-1-octen-3-ol, 7-hydroxy-3,7-dimethyloctanal, 3-nonanol, 2,6-nonadien-1-ol, *cis*-6-nonen-1-ol, 6,8-dimethylnonan-2-ol, 3-(hydroxymethyl)-2-nonanone, 2-nonen-1-ol, 2,4-nonadien-1-ol, 3,7-dimethyl-1,6-nonadien-3-ol, decanol, 9-decenol, 2-benzyl-M-dioxa-5-ol, 2-decen-1-ol, 2,4-decadien-1-ol, 4-methyl-3-decen-5-ol, 3,7,9-trimethyl-1,6-decadien-3-ol (isobutyl linallol), undecanol, 2-undecen-1-ol, 10-undecen-1-ol, 2-dodecen-1-ol, 2,4-dodecadien-1-ol, 2,7,11-trimethyl-2,6,10-dodecatrien-1-ol (farnesol), 3,7,11-trimethyl-1,6,10,-dodecatrien-3-ol, 3,7,11,15-tetramethylhexadec-2-en-1-ol (phytol), 3,7,11,15-tetramethylhexadec-1-en-3-ol (iso phytol), benzyl alcohol, p-methoxy benzyl alcohol (anisyl alcohol), *para*-cymen-7-ol (cuminy alcohol), 4-methyl benzyl alcohol, 3,4-methylenedioxy benzyl alcohol, methyl salicylate, benzyl salicylate, *cis*-3-hexenyl salicylate, n-pentyl salicylate, 2-phenylethyl salicylate, n-hexyl salicylate, 2-

methyl-5-isopropylphenol, 4-ethyl-2-methoxyphenol, 4-allyl-2-methoxyphenol (eugenol), 2-methoxy-4-(1-propenyl)phenol (isoeugenol), 4-allyl-2,6-dimethoxy-phenol, 4-tert-butylphenol, 2-ethoxy-4-methylphenol, 2-methyl-4-vinylphenol, 2-isopropyl-5-methylphenol (thymol), pentyl-*ortho*-hydroxy benzoate, ethyl 2-hydroxy-benzoate, methyl 2,4-dihydroxy-3,6-dimethylbenzoate, 3-hydroxy-5-methoxy-1-methylbenzene, 2-tert-butyl-4-methyl-1-hydroxybenzene, 1-ethoxy-2-hydroxy-4-propenylbenzene, 4-hydroxytoluene, 4-hydroxy-3-methoxybenzaldehyde, 2-ethoxy-4-hydroxybenzaldehyde, decahydro-2-naphthol, 2,5,5-trimethyl-octahydro-2-naphthol, 1,3,3-trimethyl-2-norbornanol (fenchol), 3a,4,5,6,7,7a-hexahydro-2,4-dimethyl-4,7-methano-1H-inden-5-ol, 3a,4,5,6,7,7a-hexahydro-3,4-dimethyl-4,7-methano-1H-inden-5-ol, 2-methyl-2-vinyl-5-(1-hydroxy-1-methylethyl)tetrahydrofuran, β -caryophyllene alcohol, and mixtures thereof.

Preferred pro-accords are selected from the group consisting of tris-geranyl orthoformate, tris(*cis*-3-hexen-1-yl) orthoformate, tris(phenylethyl) orthoformate, bis(citronellyl) ethyl orthoacetate, tris(citronellyl) orthoformate, tris(*cis*-6-nonenyl) orthoformate, tris(phenoxyethyl) orthoformate, tris(geranyl, neryl) orthoformate (70:30 geranyl:neryl), tris(9-decenyl) orthoformate, tris(3-methyl-5-phenylpentanyl) orthoformate, tris(6-methylheptan-2-yl) orthoformate, tris([4-(2,2,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-yl] orthoformate, tris[3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-yl] orthoformate, trismenthyl orthoformate, tris(4-isopropylcyclohexylethyl-2-yl) orthoformate, tris-(6,8-dimethylnonan-2-yl) orthoformate, tris-phenylethyl orthoacetate, tris(*cis*-3-hexen-1-yl) orthoacetate, tris(*cis*-6-nonenyl) orthoacetate, tris-citronellyl orthoacetate, bis(geranyl) benzyl orthoacetate, tris(geranyl) orthoacetate, tris(4-isopropylcyclohexylmethyl) orthoacetate, tris(benzyl) orthoacetate, tris(2,6-dimethyl-5-heptenyl) orthoacetate, bis(*cis*-3-hexen-1-yl) amyl orthoacetate, and neryl citronellyl ethyl orthobutyrate, nonadyl orthoformate, mugetanol orthoformate, osyrol orthoformate, undecavertol orthoformate and mixtures thereof.

Orthoester pro-accords and pro-fragrances and the fragrance raw materials which they are capable of delivering, all of which are suitable for inclusion in the fragrance delivery systems of the present invention, described in U.S. 6,013,618 Morelli et al., issued January 11, 2000; U.S. 5,919,752 Morelli et al., issued July 6, 1999 both of which are incorporated herein by reference.

FRAGRANCE DELIVERY SYSTEMS

The present invention also relates to fragrance raw material delivery systems which can be fully formulated and used without dilution. Preferably said delivery systems are diluted with one or more carriers. Alternatively, and in an equally preferable embodiment, the fragrance delivery systems of the present invention can be combined with other fragrance raw materials.

After formulation or combination with other fragrance raw materials and carriers, the fragrance delivery systems of the present invention can be formulated into compositions, inter alia, deodorants, shampoos, fine fragrances.

The fragrance delivery systems of the present invention comprise:

- i) optionally from about 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 99%, more preferably to about 75%, most preferably to about 50% by weight, of a cyclic aldehyde or ketone releasing pro-fragrance as described herein above;
 - ii) optionally from about 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 99%, more preferably to about 75%, most preferably to about 50% by weight, of an β -amino pro-fragrance component according to the present invention;
 - iii) optionally from about 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 99%, more preferably to about 75%, most preferably to about 50% by weight, of one or more pro-accords formed from at least one fragrance raw material, wherein said pro-acord is an orthoester; and
 - iv) optionally the balance carriers, stabilizers, and other adjunct ingredients;
- however, one compound from two of (i), (ii), or (iii) must be present.

Non-limiting examples of the fragrance delivery system of the present invention are illustrated by the following:

TABLE I

Weight %

Ingredients	1	2	3	4
β -Amino ketone pro-fragrance ¹	50	40	--	--
β -Amino ketone pro-fragrance ²	--	--	--	60
Pro-fragrance ³	25	20	--	--
Pro-fragrance ⁴	25	20	45	--
Pro-fragrance ⁵	--	--	55	20
Carrier ⁶	--	balance	--	balance

1. 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-3-N,N-bis(5-hydroxy-3-oxapentyl)-1-butanone.
2. 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-3-N-(5-hydroxy-3-oxapentyl)-1-butanone.

3. 2-(2,4-dimethyl-3-cyclohexen-1-yl)-3-(1-methylethyl)4-oxazolidinecarboxylic acid methyl ester.
4. 2-(6-methyl-5-hepten-2-yl)-3-(1-methylethyl)-4-oxazolidinecarboxylic acid methyl ester.
5. Tris(geranyl) orthoformate.
- 5 6. Ethanol.

Further examples of the use of the fragrance delivery systems of the present invention include delivery systems comprising:

- A) from about 0.1%, preferably from about 0.5%, more preferably from about 1%, yet more preferably from about 5%, most preferably from about 10% to about 100%, preferably to about 75%, more preferably to about 50% by weight, of at least two pro-fragrance or pro-accord components selected from the group comprising:
 - i) optionally from about 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 100%, more preferably to about 75%, most preferably to about 50% by weight, of a cyclic aldehyde or ketone releasing pro-fragrance as described herein above;
 - ii) optionally from about 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 100%, more preferably to about 75%, most preferably to about 50% by weight, of an β -amino pro-fragrance component according to the present invention;
 - iii) optionally from about 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 99%, more preferably to about 75%, most preferably to about 50% by weight, of one or more pro-accords formed from at least one fragrance raw material, wherein said pro-accord is an orthoester;
 - iv) the balance carriers, stabilizers, and other adjunct ingredients; and
- B) optionally from about 0.01%, preferably from about 0.5%, more preferably from about 1%, yet more preferably from about 5%, most preferably from about 10% to about 99%, preferably to about 75%, more preferably to about 50% by weight, a fragrance raw material component comprising:

- i) optionally at least 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 100%, more preferably to about 75%, most preferably to about 50% by weight, of a mixture of one or more base note fragrances;
- 5 ii) optionally at least 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 100%, more preferably to about 75%, most preferably to about 50% by weight, of a mixture of one or more top or middle note fragrances;
- iii) optionally the balance carriers, fixatives, and other adjunct ingredients.

10 A non-limiting example of a preferred embodiment of the fragrance delivery system of the present invention includes:

- A) from about 0.1%, preferably from about 0.5%, more preferably from about 1%, yet more preferably from about 5%, most preferably from about 10% to about 100%, preferably to about 75%, more preferably to about 50% by weight, of at least two pro-fragrance or pro-accord components selected from the group comprising:
- 15

- i) optionally from about 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 100%, more preferably to about 75%, most preferably to about 50% by weight, of a cyclic aldehyde or ketone releasing pro-fragrance as described herein above;
- 20 ii) optionally from about 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 100%, more preferably to about 75%, most preferably to about 50% by weight, of an β -amino ketone pro-fragrance component according to the present invention;
- 25 iii) optionally from about 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 99%, more preferably to about 75%, most preferably to about 50% by weight, of one or more pro-accords formed from at least one fragrance raw material, wherein said pro-accord is selected from the group consisting of acetals, ketals, orthoesters, orthocarbonates, and mixtures thereof, each pro-accord releasing upon hydrolysis said fragrance raw material from which it is formed, said fragrance raw materials selected
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from the group consisting of primary, secondary, and tertiary alcohols, aldehydes, ketones, esters, carbonates, and mixtures thereof, provided at least one pro-accord:

- a) is formed from at least one fragrance raw material having a molecular weight greater than or equal to about 100 g/mol;
 - b) has a fragrance release half-life of greater than or equal to about 0.1 hours at pH 5.3 and less than or equal to about 12 hours at pH 2.5 when measured in NaH_2PO_4 buffer;
 - iv) the balance carriers, stabilizers, and other adjunct ingredients; and
- B) optionally from about 0.01%, preferably from about 0.5%, more preferably from about 1%, yet more preferably from about 5%, most preferably from about 10% to about 99%, preferably to about 75%, more preferably to about 50% by weight, of a fragrance raw material component comprising:
- i) optionally at least 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 100%, more preferably to about 75%, most preferably to about 50% by weight, of a mixture of one or more base note fragrances;
 - ii) optionally at least 0.01%, preferably from about 0.5%, more preferably from about 5%, most preferably from about 25% to about 100%, more preferably to about 75%, most preferably to about 50% by weight, of a mixture of one or more top or middle note fragrances;
 - iii) optionally the balance carriers, fixatives, and other adjunct ingredients.

When used the fragrance delivery systems of the present invention will comprise from about 0.1%, preferably from about 1% to about 100%, preferably to about 85% of the composition depending upon the execution. For example, a fine fragrance may comprise 100% by weight, of a fragrance delivery as described herein, whereas a body lotion or cream may comprise from about 1% to about 5% by weight, of the fragrance delivery system.

For the purposes of the fragrance delivery systems of the present invention, a "pro-accord which comprises n fragrance raw materials but which releases $n+1$ fragrance raw materials" is defined as "a compound which is prepared from one or more fragrance raw materials, said fragrance raw material being chemically transformed into a "releasable form" such that when said releasable form breaks down, the original fragrance raw material is released as well as at least one other fragrance raw material which was not a starting material used in forming the releasable form". The term "releasable form" is defined herein as a "pro-fragrance or pro-accord

compound, which ever form is applicable". Non-limiting examples of "releasable forms" or pro-accords which satisfy the $n + 1$ requirement are as follows.

Preferably the pro-accords of the present invention are orthoesters and orthocarbonates which deliver $n + 1$ fragrance raw materials when the "pro-accord" has been formed from n fragrance raw materials. These "Increased Release" pro-accords are preferably formate, acetate, propionate, and benzoate orthoesters. Any fragrance raw material may be used to form the "increased release" pro-accord provided the final pro-accord:

- a) has a molecular weight greater than or equal to about 300 g/mol;
- b) has a molecular weight at least two times greater than the lowest molecular weight fragrance raw material which comprises said pro-accord; and
- c) has a fragrance release half-life greater than or equal to about 0.1 hours when measured in NaH_2PO_4 buffer at pH 5.3 and less than about 12 hours when measured in NaH_2PO_4 buffer at pH 2.5.

The value of the index n is an integer from 1 to 3.

When present the "increased release" pro-accords comprise at least 0.01% of the increased fragrance retention composition, preferably at least about 0.1% more preferably at least about 0.5% by weight, of said composition. More than one "increased release" pro-accords may be combined together as described herein above to provide a complex perfume mixture or accord.

The pro-accord tris(9-decenyl) orthoformate is prepared by treating 9-decenol (i.e., Rosalva), which is a fragrance raw material as defined herein, with a suitable amount of triethyl orthoformate, not a fragrance raw material as defined herein, in the presence of an acid catalyst optionally in the presence of a solvent. Tris(9-decenyl) when exposed to suitable conditions (e.g., exposure to the acid mantle of human skin) breaks down to release a mixture of 9-decenol and 9-decenyl formate, both of which are fragrance raw materials. Therefore, one fragrance raw material is used to prepare a releasable form (pro-accord) of two fragrance raw materials.

The pro-accord 3,7-dimethyl-1,6-octadien-3-yl 3-(β -naphthyl)-3-oxo-propionate, which is a β -ketoester pro-accord, is prepared by treating 3,7-dimethyl-1,6-octadien-3-ol (linalool), which is a fragrance raw material according to the present invention, with diketene under suitable conditions to form intermediate 3,7-dimethyl-1,6-octadien-3-yl 3-oxo-butyrate, which is subsequently treated with 2-naphthoyl chloride to yield the pro-accord. 3,7-Dimethyl-1,6-octadien-3-yl 3-(β -naphthyl)-3-oxo-propionate when exposed to suitable conditions (e.g., exposure to nascent moisture) breaks down to release a mixture of linalool and methyl β -naphthyl ketone, both of which are fragrance raw materials as defined herein.

As described herein above, an optional component of the fragrance delivery systems of the present invention are pro-fragrances or pro-accords which are not heterocyclic aldehyde and/or ketone releasing pro-fragrances. The optional pro-accords or pro-fragrances are equally functional in either personal care compositions *inter alia* lotions, creams, deodorants or personal fragrance compositions *inter alia* fine fragrances, perfumes.

Preferred optional pro-accords and/or pro-fragrances include, but are not limited to, orthocarbonates, acetals, ketals, ortholactones, and β -ketoesters.

Non-limiting examples of optional orthocarbonates which are suitable for use in the fragrance delivery systems of the present invention include bis(ethyl) bis(geranyl) orthocarbonate, bis(ethyl) bis(phenylethyl) orthocarbonate, bis(ethyl) bis(*cis*-3-hexenyl) orthocarbonate, bis(ethyl) bis(citronellyl) orthocarbonate, bis(ethyl) bis(linalyl) orthocarbonate, bis(ethyl) bis(menthyl) orthocarbonate, bis(dodecyl) bis(geranyl) orthocarbonate, and bis(dodecyl) bis(phenylethyl) orthocarbonate.

Non-limiting examples of optional acetals which are suitable for use in the fragrance delivery systems of the present invention include bis(*cis*-3-hexenyl) vanillin, bis(geranyl) cinnamaldehyde acetal, bis(2-phenylethyl) anisaldehyde acetal, bis(citronellyl) cyclamen aldehyde acetal, and bis(citronellyl) citral acetal.

Non-limiting examples of optional ketals which are suitable for use in the fragrance delivery systems of the present invention include bis(linalyl) β -ionone ketal, bis(dihydromyrcenyl) α -damascone ketal, bis(linalyl) 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone ketal, bis(dihydromyrcenyl) β -ionone ketal, and bis(citronellyl) *cis*-jasmone ketal.

Non-limiting examples of optional β -ketoesters which are suitable for use in the fragrance delivery systems of the present invention include 2,6-dimethyl-7-octen-2-yl 3-(4-methoxyphenyl)-3-oxo-propionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(α -naphthyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-(4-methoxyphenyl)-3-oxo-propionate, *cis* 3-hexen-1-yl 3-(β -naphthyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-(nonanyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-oxo-butyrate, 3,7-dimethyl-1,6-octadien-3-yl 3-oxo-butyrate, 2,6-dimethyl-7-octen-2-yl 3-(β -naphthyl)-3-oxo-2-methylpropionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(β -naphthyl)-3-oxo-2,2-dimethylpropionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(β -naphthyl)-3-oxo-2-methylpropionate, 3,7-dimethyl-2,6-octadienyl 3-(β -naphthyl)-3-oxo-propionate, and 3,7-dimethyl-2,6-octadienyl 3-heptyl-3-oxo-propionate.

An example of a fragrance delivery system according to the present invention comprises:

- a) from about 0.1% by weight, of a β -amino ketone pro-fragrance selected from the group consisting of 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-3-N,N-bis(5-hydroxy-3-oxapentyl)-1-butanone, 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-3-N,N-bis(2-hydroxyethyl)-1-butanone, 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-3-N-(5-hydroxy-3-oxapentyl)-1-butanone, and mixtures thereof;
- b) from about 0.2% by weight, of one or more aldehyde releasing pro-fragrances, for example, 2-(6-methyl-5-hepten-2-yl)-3-(1-methylethyl)-4-oxazikudubecarboxylic acid methyl ester, 2-(2,4-dimethyl-3-cyclohexen-1-yl)-3-(1-methylethyl)-4-oxazolidinecarboxylic acid methyl ester;
- c) optionally from about 0.1% by weight, of one or more alcohol releasing pro-fragrances; preferably an alcohol releasing pro-accord, for example, geranyl orthoformate;
- d) from about 0.1% by weight, of one or more fragrance raw materials, for example, lillial, γ -decalactone;
- e) optionally, from about 1% by weight, of pre-blended perfume ingredients of fragrance raw material accords; and
- f) the balance carriers.

A non-limiting example of an alcohol releasing pro-accord admixture which is suitable for use in the fragrance delivery systems of the present invention comprises:

- i) from about 0.5% to about 5% by weight, of nonadyl orthoformate;
- ii) from about 1.5% to about 5% by weight, of mugetanol orthoformate;
- iii) from about 1.5% to about 5% by weight, of osyrol orthoformate; and
- iv) from about 1% to about 10% by weight, of benzyl orthoacetate.

Fragrance Release Half-life

One aspect of the present invention which is a key element in providing the formulator with a method for determining the manner in which a pro-fragrance according to the present invention releases its fragrance raw material, is the measurement of the pro-fragrance "Fragrance Release Half-Life, (FRHL). The pro-fragrances useful in the personal care compositions of the present invention generally have a delayed release of final fragrance raw material in order to achieve the increased fragrance longevity benefits described herein. However, the pro-fragrances generally also deliver the fragrance raw materials during a time period useful to the formulator, for example, within a time period desirable to the consumer.

For the purposes of the present invention the pro-accords generally have a FRHL of less than or equal to 12 hours when measured in NaH_2PO_4 buffer at pH 2.5 and greater than or equal

to 0.1 hour when measured in NaH_2PO_4 buffer at pH 5.3. The "Fragrance Release Half-life" is defined herein as follows.

Pro-fragrances deliver their corresponding mixture of fragrance raw materials or fragrance accords according to the equation:



wherein the fragrance raw material which is released may be released as a single component or a multiple fragrance raw material accord.

The rate at which the fragrance is released is defined by the formula:

$$\text{Rate} = k[\text{Pro-fragrance}]$$

and can be further expressed by the formula:

$$-\frac{d[\text{Pro-fragrance}]}{dt} = k[\text{Pro-fragrance}]$$

wherein k is the release rate constant and $[\text{Pro-fragrance}]$ is the concentration of pro-fragrance. For the purposes of the present invention the "Fragrance Release Half-life", $t_{1/2}$, is related to the release rate constant by the formula:

$$t_{1/2} = \frac{0.693}{k}$$

and this relationship is used for the purposes of the present invention to determine the "FRHL".

Due to the hydrophobic nature of some pro-accords, it is necessary to conduct the determination of $t_{1/2}$ and k in a mixture of 90/10 dioxane/phosphate buffered water. The phosphate buffered water is prepared by admixing 3.95 mL of 85% phosphoric acid (H_3PO_4) and 24 g of sodium dihydrogen phosphate (NaH_2PO_4) with one liter of water. The pH of this solution is approximately 2.5. Next 10 mL of the phosphate buffer is admixed with 90 mL of dioxane and the pro-fragrance to be analyzed is added. The hydrolysis kinetics are then monitored by conventional HPLC at 30° C.

In some instances, it is desirable to formulate a fragrance delivery system having one or more pro-fragrances which deliver a rapid release of fragrance raw material in addition to the delayed onset of a fragrance. In such cases the hydrolysis rate, and therefore the determination of $t_{1/2}$ must be measured in a buffer system which can accommodate this more rapid hydrolysis rate.

The pro-fragrances of the present invention are stable under pH conditions encountered in the formulation and storage of fine perfume, personal care and personal hygiene articles which have a pH of from about 7.1 to 11.5, and during solution-use of such products. Due to their high molecular weight and hydrophobicity, these pro-fragrances and/or pro-accords remain deposited upon skin even when exposed to water (i.e. when formulated into a sun screen). Because the pro-fragrances are subject to hydrolysis when the pH is reduced, they hydrolyze to release their component fragrance compounds when applied to skin or are exposed even to reduced pH such as present in air and humidity. The reduction in pH should be at least 0.1, preferably at least about 0.5 units. Preferably the pH is reduced by at least 0.5 units to a pH of 7.5 or less, more preferably 6.9 or less. Preferably, the solution in which the pro-accord is applied is alkaline.

Odor Value

The pro-fragrances of the present invention typically have an Odor Value greater than or equal to about 1, preferably greater than or equal to about 5, more preferably greater than or equal to about 10. The term "Odor Value" is defined by the following formula:

$$OV = \frac{[\text{Concentration of FRM}]}{ODT}$$

wherein OV is the odor value of the fragrance raw material released upon the skin by the pro-accord. The odor value is the concentration of the fragrance raw material, FRM, on the skin surface divided by the Odor Detection Threshold, ODT. The term "level of noticeability" is often applied to and/or substituted for the term "odor value".

Odor Detection Threshold

For the purposes of the present invention the term "odor detection threshold" is defined as the level at which a fragrance raw material is perceptible to the average human. The odor detection threshold (ODT) of the compositions of the present invention are preferably measured by carefully controlled gas chromatograph (GC) conditions as described hereinbelow. The preferred fragrance raw materials of the present invention have an ODT of at least about 100 part per billion (ppb), more preferably 10 ppb, most preferably 1 ppb. Fragrance raw materials having an ODT greater than 10 parts per million (ppm) are typically avoided unless useful as an adjunct ingredient, for example, as an adjunct alcohol when adjusting the fragrance release half-life of an orthoester.

Determination of Odor Detection Thresholds is as follows. A gas chromatograph is characterized to determine the exact volume of material injected by a syringe, the precise split

ratio, and the hydrocarbon response using a hydrocarbon standard of known concentration and chain-length distribution. The air flow rate is accurately measured and, assuming the duration of a human inhalation to last 0.02 minutes, the sampled volume is calculated. Since the precise concentration at the detector at any point in time is known, the mass per volume inhaled is known and hence the concentration of material. To determine whether a material has a threshold below 10 ppb, solutions are delivered to the sniff port at the back-calculated concentration. A panelist sniffs the GC effluent and identifies the retention time when odor is noticed. The average over all panelists determines the threshold of noticeability or ODT. The necessary amount of analyte is injected onto the column to achieve a 10 ppb concentration at the detector. Typical gas chromatograph parameters for determining odor detection thresholds are listed below.

GC: 5890 Series II with FID detector 7673 Autosampler

Column: J&W Scientific DB-1, length 30 m, i.d. 0.25 mm, film thickness 1 μ m.

Split Injection: 17/1 split ratio

Autosampler: 1.13 μ l/injection

Column flow: 1.10 mL/min

Air flow: 345 mL/min

Inlet temperature: 245° C

Detector temperature: 285° C

Temperature Information:

Initial temperature: 50° C

Rate: 5° C/min

Final temperature: 280° C

Final time: 6 min

Leading assumptions: 0.02 minutes per sniff and that GC air adds to sample dilution.

Skin Performance Index

Although a pro-fragrance or pro-accord may comprise a fragrance release half-life which ensures delivery of a fragrance raw material during a period of time useful to the formulator, unless the fragrance raw materials which comprise said fragrance delivery system have ODT values large enough to be perceived by the user, the formulator will be compelled to use an inordinate amount of material to achieve a suitable fragrance level.

The pro-fragrances of the present invention have a Skin Performance Index (SPI) greater than or equal to 0.1, preferably greater than or equal to 0.5. The Skin Performance Index is defined by the following:

$$SPI = \frac{[\text{Odor Value}]^*}{t_{1/2}}$$

wherein the term [Odor Value]* is the estimated concentration of the fragrance raw material in the headspace above a solution of the fragrance raw material as measured in a 1% solution of ethanol, and $t_{1/2}$ is the fragrance release half-life measured at pH 5.3 in the above described buffer. For the purposes of the present invention, the $t_{1/2}$ of the SPI is measured at 5.3 and the value of the fragrance release half-life is preferably from 0.1 hours to 60 hours.

The [Odor Value]* is an estimation of the vapor pressure of the fragrance raw material using empirically determined KOVATS indices. "The Vapor Pressures of Pure Substances", T. Boublik et al., Elsevier, New York (1973) incorporated herein by reference, describes an index line for normal alkanes wherein C_{10} is equal to 30,000 ppb, C_{12} is equal to 3,000 ppb, C_{14} is equal to 300 ppb, C_{16} is equal to 30 ppb, etc. Using these values as reference standards, the KOVATS index of a fragrance raw material is obtained from gas chromatographic analysis of the FRM and the experimental index is then used to determine the relative vapor pressure and hence the head space concentration of the fragrance raw material.

"New Method for Estimating Vapor Pressure by the Use of Gas Chromatography" *J. Chromatography A*, 79 p 123-129, (1996) and "Simple and Versatile Injection System for Capillary Gas Chromatographic Columns: Performance Evaluation of a System Including Mass Spectrometric and Light Pipe Fourier-Transform Infrared Detection", *J. Chromatography A*, 713, p 201-215, (1996) included herein by reference, further describe methods and techniques suitable for use in determining the vapor pressure and head space concentration of FRM's as they relate to the term [Odor Value]* of the present invention.

Using the criteria set forth in the present invention *inter alia* fragrance release half-life, odor value, odor detection threshold, skin performance index, the formulator is able to fashion an aldehyde or ketone releasing cyclic pro-fragrance. By manipulation of the R^2 , R^3 , R^4 , R^5 and R^6 units of the cyclic pro-fragrances of the present invention, the release rate of either an aldehyde or ketone fragrance raw material can be adjusted. Several different pro-fragrances which release the same fragrance raw material, but at differing rates or levels, can be admixed to further prolong or extend the period of fragrance raw material delivery.

When present, the carriers, fixatives, or stabilizers will comprise the balance of the compositions. Typical carriers are methanol, ethanol (preferred), iso-propanol, polyethylene glycol, as well as water in some instances, especially as a vehicle to deliver materials which provide reserve alkalinity to the fragrance delivery system. Fixatives serve to lower the volatility

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of certain top and middle notes in order to extend their contact time on skin. Adjunct ingredients include perfume raw material components which are essential oils and are therefore not a single chemical entity. In addition, the adjunct ingredients may be mixtures of materials which serve a purpose in addition to providing a pleasurable odor (i.e., an astringent in a personal hygiene article).

The formulators, in addition to selected fragrance raw materials, can combine a pre-blended fragrance with the pro-fragrances of the present invention. For the purposes of the present invention the term "pre-blended fragrance" is defined as an existing fragrance accord, commercially available or otherwise, which is enhanced by or in turn enhances the fragrance delivered by the pro-fragrances and/or pro-accords which comprise the balance of the fragrance delivery system. For example, an existing fragrance accord may be suitable in the short term but due to differential evaporation of the most volatile components, high notes, *inter alia*, the fragrance diminishes or the bouquet shifts. Therefore, pro-fragrances and pro-accords are combined which will release said volatile components thereby sustaining the complete fragrance accord.

The following is a non-limiting example of a β -amino ketone pro-fragrance according to the present invention.

EXAMPLE 5

1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-3-N-(2-hydroxyethyl)-N-phenylmethyl-1-butanone

The damascone releasing β -amino ketone pro-fragrance adduct is prepared by stirring 1 equivalent of δ damascone with 2 equivalents of *N*-benzylethanolamine until complete as indicated suitable analytical method *inter alia*, thin layer chromatography, ^1H NMR. The product is purified by column chromatography on Aluminum Oxide (activated, basic, Brockman I, standard grade, 150 mesh, 58 angstrom) using a mobile phase consisting of 50% hexane, 49% chloroform and 1% triethylamine. Solvents are removed *in vacuo* and the product is placed under high vacuum (0.10 mm Hg) for 24 hours with stirring to remove any residual solvent to yield the desired β -amino ketone pro-fragrance.

The following are examples of fine fragrance compositions which comprise the fragrance delivery system of the present invention.

TABLE II

Weight %

Ingredients	6	7	8	9
β -Amino ketone pro-fragrance ¹	0.4	0.8	--	--

β -Amino ketone pro-fragrance ²	--	--	--	0.6
Pro-fragrance ³	0.2	0.4	--	--
Pro-fragrance ⁴	0.2	0.4	0.5	--
Pro-fragrance ⁵	--	--	0.6	0.2
Pro-fragrance ⁶	--	--	--	0.2
Pre-formulated accords ⁷	14.0	14.0	14.0	14.0
Fragrance raw material ⁸	1.98	1.98	--	--
Fragrance raw material ⁹	0.02	0.02	--	--
Carrier ¹⁰	balance	balance	balance	balance

1. 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-3-N,N-bis(5-hydroxy-3-oxapentyl)-1-butanone.

2. 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-3-N-(5-hydroxy-3-oxapentyl)-1-butanone.

3. 2-(2,4-dimethyl-3-cyclohexen-1-yl)-3-(1-methylethyl)4-oxazolidinecarboxylic acid methyl ester.

5 4. 2-(6-methyl-5-hepten-2-yl)-3-(1-methylethyl)-4-oxazolidinecarboxylic acid methyl ester.

5. Tris(geranyl) orthoformate.

6. Benzyl bis(geranyl) orthoformate.

7. Admixture of one or more fragrance raw materials which is enhanced by the presence of said fragrance delivery system.

10 8. Lillial.

9. γ -decalactone.

10. Ethanol.

TABLE III

Weight %

Ingredients	10	11	12	13
β -Amino ketone pro-fragrance ¹	--	--	--	0.6
β -Amino ketone pro-fragrance ²	0.4	0.8	--	--
Pro-fragrance ³	0.2	0.3	--	--
Pro-fragrance ⁴	0.2	0.3	1.0	--
Pro-fragrance ⁵	--	--	0.8	--
Pro-fragrance ⁶	--	--	--	0.3
Pre-formulated accords ⁷	13.8	13.8	13.5	14.0
Fragrance raw material ⁸	1.98	1.0	--	2.0

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Fragrance raw material ⁹	0.02	0.04	0.01	--
Carrier ¹⁰	balance	balance	balance	balance

1. 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-3-N,N-bis(5-hydroxy-3-oxapentyl)-1-butanone.
2. 1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-3-N-(5-hydroxy-3-oxapentyl)-1-butanone.
3. 2-(2,4-dimethyl-3-cyclohexen-1-yl)-3-(1-methylethyl)4-oxazolidinecarboxylic acid methyl ester.
- 5 4. 2-(6-methyl-5-hepten-2-yl)-3-(1-methylethyl)-4-oxazolidinecarboxylic acid methyl ester.
5. Tris(geranyl) orthoformate.
6. Benzyl bis(geranyl) orthoformate.
7. Admixture of one or more fragrance raw materials which is enhanced by the presence of said fragrance delivery system.
- 10 8. Lillial.
9. γ -decalactone.
10. Admixtures of ethanol and water ranging from about 100:0 to 50:50 by weight.

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